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## V.

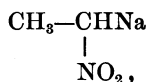
CONTRIBUTIONS FROM THE KENT CHEMICAL LABORATORY  
OF THE UNIVERSITY OF CHICAGO.

ON THE CONSTITUTION OF THE NITROPARAFFINE  
SALTS.

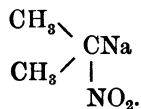
By J. U. NEF.

Presented May 9, 1894.

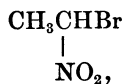
VICTOR MEYER, who discovered the nitro fatty compounds, has, as is well known, shown that the primary and secondary nitroparaffines differ from the corresponding tertiary derivatives, as well as from the aromatic nitro bodies, especially in the fact that they possess acid properties. He has explained this very noteworthy character by the assumption that the introduction of the nitro group exerts an "acid making" influence on the molecule, which, however, extends only to hydrogen atoms bound to the same carbon atom as the negative radical. He therefore supposes \* sodic nitroethane to possess the constitution represented by the formula



and, in an analogous manner, he represents the sodium salt of secondary nitropropane by the formula



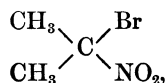
The fact that these salts, when treated with bromine, are converted into bromnitroethane,



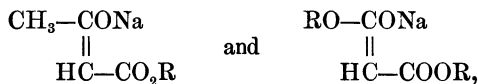

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\* Ann. Chem. (Liebig), CLXXI. 28, 48.

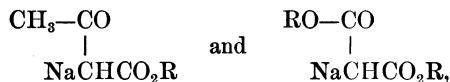
a strong acid, and into bromnitropropane,



a neutral body, seems at first to be an argument in favor of this hypothesis. I have, however, already pointed out\* that one is not justified in drawing from this reaction such a conclusion with regard to the nature of the sodium salts, and have further demonstrated† that the hypothesis of the acid making influence of negative groups or radicals has absolutely no justification, and is entirely illogical. That this hypothesis is no longer tenable in many cases where it has hitherto been accepted is clear. That the sodium salts of acetoacetic ether and of malonic ether possess a structure which must be represented by the formulæ



and not, as previously supposed, by the formulæ

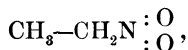


can now be regarded as settled experimentally beyond a doubt.‡

For these reasons it is almost self-evident that the metal in the nitroparaffine salts cannot be bound directly to carbon, and is in all probability bound to oxygen; and the following experiments prove this in a most satisfactory manner.

#### I. DECOMPOSITION OF PRIMARY AND SECONDARY NITROPARAFFINE SALTS BY MEANS OF ACIDS.

Assuming that nitroethane possesses the constitution

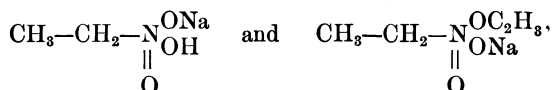


\* Amer. Chem. Journal, XIII. 427.

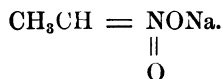
† These Proceedings, XXVII. 157.

‡ Ann. Chem. (Liebig), CCLVIII. 261, CCLXVI. 52, CCLXXVI. 200, and CCLXXVII. 59.

it is very well possible \* that on treating it with sodic hydrate or with sodium ethylate, an addition of these reagents to the nitro group takes place, forming thus the products,



which by loss of water or alcohol must give sodic nitroethane of the constitution



This reaction is entirely analogous to the formation of sodic malonic ether from malonic ether and sodium ethylate,† the only difference being in the fact that sodic malonic ether is instantly decomposed by water, regenerating the ester and forming sodic hydrate,‡ whereas sodic nitroethane dissolves in water without decomposition.

In favor of this interpretation of salt formation can be adduced the fact that many higher members of the nitroparaffine series, which ought, like nitroethane, to possess acid properties, dissolve only with great difficulty and on prolonged treatment in very concentrated sodic hydrate; § i. e. they possess very weak acid properties and were consequently long considered to be neutral substances, || — a fact which, as V. Meyer also observes, ¶ is very noteworthy. If, however, the salt formation depends on the addition of sodic hydrate to the nitro group and subsequent loss of water, the peculiar and unexpected behavior observed in these cases is easily comprehensible; the first members of the nitroparaffine series are soluble in water, and thus more easily attacked by sodic hydrate, whereas the higher members are insoluble in water.

Since, according to this conception of the nitroparaffine salts, they do not possess a constitution analogous to that of the free nitro compounds, it does not of necessity follow, especially since the salts are soluble without decomposition in water, that these salts can be con-

\* These Proceedings, XXVII. 150–158.

† Ann. Chem. (Liebig), CCLXVI. 67, CCLXXVI. 244.

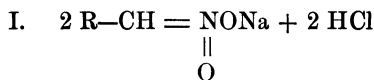
‡ Ibid., CCLXVI. 113.

§ Ibid., CLXXV. 135, 144; Züblin, Ber. d. chem. Ges., X. 2083; Konowalow, Ber. d. chem. Ges., XXV. Ref. 108.

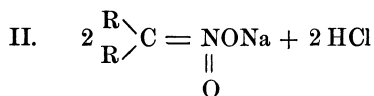
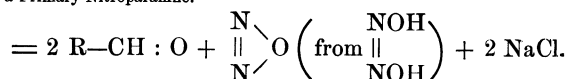
|| Ber. d. chem. Ges., V. 203; Ann. Chem. (Liebig), CLXXI. 44.

¶ Lehrbuch, p. 205.

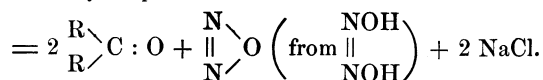
verted back again completely into the free nitro bodies from which they were obtained. The first problem therefore was to determine this point by experiment, and it was found that under no condition is it possible to convert these salts back again completely into the corresponding free nitro compounds. On adding an aqueous solution of a sodium salt of a nitroparaffine to cold dilute sulphuric or hydrochloric acid, not a trace of the nitroalkyle is regenerated, but a more or less smooth decomposition into nitrous oxide and an aldehyde or ketone takes place, according to one of the following equations:



Sodium Salt of a Primary Nitroparaffine.

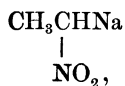


Sodium Salt of a Secondary Nitroparaffine.



This new very noteworthy decomposition of nitroparaffine salts, which always takes place, no matter how the experiment is carried out, has been overlooked by V. Meyer and by all who have worked with these compounds. V. Meyer states repeatedly that it is possible to regenerate the free nitroparaffine from its sodium salt or from a caustic alkaline solution, — a fact which is only true to a limited extent (see below). Decomposition always takes place according to one or the other of the above equations, and this fact alone proves that the nitroparaffine salts cannot possibly have a constitution analogous to that of the free nitroalkyles.

If, for example, sodic nitroethane possessed the constitution



it ought to be possible to convert it quantitatively into  $\text{CH}_3-\text{CH}_2\text{NO}_2$  by addition to dilute sulphuric acid, just as sodium acetate goes over

completely into acetic acid on similar treatment. As a matter of fact, not a trace of nitroethane is formed.

*Decomposition of Sodid Nitroethane by Acids.*—Sodid nitroethane can be obtained from nitroethane by treating it in absolute ethereal solution with sodium wire, or by means of alcoholic sodic hydrate, according to the method of V. Meyer.\* It is, however, best formed by addition of an alcoholic solution of sodic ethylate to an alcoholic solution of nitroethane. The salt is filtered off, well washed with alcohol, and dried on clay plates and over sulphuric acid in a vacuum; 30 grams nitroethane gave regularly 33 grams sodium salt. A complete analysis of the salt is not possible, because it explodes on heating with cupric oxide.

0.3035 gram substance gave 0.2225 gram  $\text{Na}_2\text{SO}_4$ .

	Theory for $\text{C}_2\text{H}_4\text{NO}_2\text{Na}$ .	Found.
Na	23.71	23.74

On adding quickly an aqueous solution of sodid nitroethane (1 part to 10 parts  $\text{H}_2\text{O}$ ) to cold dilute sulphuric acid (1 : 5), using for one gram salt about 15 to 20 c.cm. of the acid, decomposition takes place into nitrous oxide and acetaldehyde; the reaction takes place with much evolution of heat, the solution becomes colored green, and not a trace of nitroethane is regenerated. The experiment can be carried out quantitatively as follows: 15 to 20 c.cm. of dilute sulphuric acid are brought into a small distilling flask which is provided with a separatory funnel, and is connected on the one hand with a carbonic acid generator, and on the other with a Schiff's nitrometer. Air is first expelled from the apparatus by means of carbon dioxide (passed over heated copper), and then the aqueous solution of sodid nitroethane is quickly added by means of the separatory funnel and well washed down with water. The distilling flask is then heated to boiling and the nitrous oxide driven over, by a current of carbonic acid, into the azotometer. The aldehyde which is formed is absorbed by the caustic potash solution (1 : 2) in the nitrometer, which was saturated previous to the experiment with nitrous oxide.

0.7 gram substance gave 77 c.cm.  $\text{N}_2\text{O}$  at  $15^\circ$  and 754 mm., corresponding to 89.4% of the theoretical amount.

1.0 gram substance gave 105 c.cm.  $\text{N}_2\text{O}$  at  $16^\circ$  and 748 mm., corresponding to 84.6% of the theoretical amount.

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\* Ann. Chem (Liebig), CLXXI. 29.

That nitrous oxide was present was shown by its characteristic reactions, and by passing a known volume of the gas over heated copper, whereby an equal volume of nitrogen was obtained.

In order to determine the amount of acetaldehyde quantitatively, the same apparatus is used except that the distilling flask, instead of being connected with an azotometer, is connected with a condenser and a well cooled receiver containing water. About one half of the solution in the distilling flask is then boiled off, and the distillate in the receiver is treated with powdered calcic carbonate to remove traces of acetic acid, and then again distilled over. The second distillate thus obtained is perfectly neutral to test paper, and is heated for four hours in a sealed tube at 100° with an excess of silver oxide.\* The silver acetate formed is boiled out with water, and the amount determined by evaporating the aqueous solution.

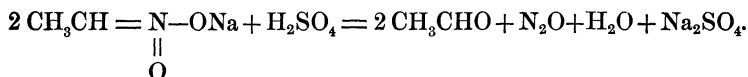
1.5 grams sodic nitroethane gave 1.8 grams silver acetate, or 69.7% of the theoretical amount.

A portion of the silver acetate, recrystallized from water and dried at 80–90°, gave the following result on analysis :

0.3552 gram substance gave 0.2297 gram silver.

	Theory for CH <sub>3</sub> CO <sub>2</sub> Ag	Found.
Ag	64.67	64.67

Sodic nitroethane has thus been split pretty smoothly, on treatment with an acid, according to the following equation :

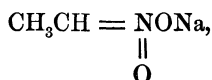


The amount of acetaldehyde obtained (69.7% of the theory) is undoubtedly somewhat less than the actual amount formed in the reaction, since a slight loss of aldehyde can hardly be avoided in the above operations. It was shown qualitatively that nitrous acid, acetic acid, and hydroxylamine are side products in the above reaction. Entirely analogous results are obtained if hydrochloric acid, instead of sulphuric acid, is used in the reaction.

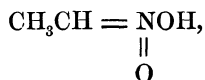
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\* A preliminary experiment with pure acetaldehyde showed that this method is well adapted for the quantitative determination of aldehyde. 1 gram acetaldehyde (bpt. 23°), 20 c.cm. water, and 8.3 grams silver oxide, heated in a sealed tube at 100° for one hour, gave 3.1 grams silver acetate corresponding to 81.7 per cent of the theory. Traces of unchanged aldehyde were noticed on opening the sealed tube.

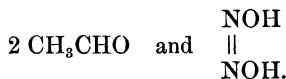
The following explanation of this noteworthy decomposition of sodic nitroethane is extremely probable, especially because of facts to be presented later in this paper. On the addition of sodic nitroethane,



to a dilute acid, there is first formed the product



which must be a strong oxidizing agent, and which therefore splits, just as in analogous cases to be presented below, by intramolecular oxidation into



V. Meyer states\* that on addition of an acid to aqueous sodic nitroethane, or to a caustic alkaline solution of nitroethane, free nitroethane is formed. Later he mentions† that acids never regenerate the entire amount of nitroethane from a solution of this substance in caustic potash, and that ethylnitrolic acid is always formed in small quantity. He seems never to have noticed a decomposition into acetaldehyde and nitrous oxide, which however always takes place, as is evident from the following experiments.

20 grams nitroethane are dissolved in a solution of 20 grams caustic potash ( $1\frac{1}{2}$  molecules) in 300 c.cm. of water: the smell of nitroethane is still distinctly noticeable. To this solution is added very slowly dilute sulphuric acid, taking care to cool well with water. As soon as the solution becomes acid, it is colored greenish, and a gas evolution ( $\text{N}_2\text{O}$ ) and strong smell of acetaldehyde are noticed. Since no nitroethane separates out, the solution is extracted three times with ether. The ethereal solution, after drying with calcic chloride, is then carefully fractionated; the lower boiling portions smell strongly of acetaldehyde. 7.2 grams oil were obtained, boiling between  $112^\circ$  and  $118^\circ$ , which, redistilled, gave 5.2 grams, boiling between  $112^\circ$  and  $116^\circ$ . The oil, although it smells of aldehyde, undoubtedly consists chiefly

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\* Ann. Chem. (Liebig), CLXXI. 27-30. Cf. also Ber. d. chem. Ges., V. 514-516.

† Ann. Chem. (Liebig), CLXXV. 88-90.



of nitroethane, since on treatment with sodic nitrite 5 grams of ethylnitrolic acid were obtained from it.

An entirely analogous result is obtained on adding very slowly dilute sulphuric or hydrochloric acid to an aqueous solution of sodic nitroethane (made by means of sodium ethylate).

It is also possible to obtain traces of nitroethane on adding very slowly an aqueous solution of the sodium salt to dilute sulphuric acid, cooled with pieces of ice. The chief reaction in this case is, however, decomposition into acetaldehyde and nitrous oxide.

*Decomposition of Nitroethane-mercuric-chloride by means of Acids.*

Nitroethane-mercuric-chloride was obtained by addition of corrosive sublimate (one molecule) to an aqueous solution of sodic nitroethane. Since V. Meyer determined only the percentage of chlorine and mercury in the salt,\* the substance, after drying for 24 hours in a vacuum, was analyzed for carbon and hydrogen.

0.6849 gram substance gave 0.1949 gram  $\text{CO}_2$  and 0.0813 gram  $\text{H}_2\text{O}$ .

	Theory for $\text{C}_2\text{H}_4\text{NO}_2\text{HgCl}$	Found.
C	7.75	7.76
H	1.30	1.34

The former statements concerning the properties of this salt could be confirmed except in one particular. V. Meyer mentions\* that acids regenerate nitroethane. I found it impossible, under any condition, to obtain from this salt even a trace of nitroethane.

Dilute nitric acid and sulphuric acid act upon the salt very slowly in the cold, forming acetaldehyde and nitrous oxide: dilute hydrochloric acid reacts with great violence upon it, decomposing it into nitrous oxide and acetaldehyde. A large amount of the mercury salt, suspended in water, was treated in the cold with hydrogen sulphide, and thereupon the solution was partially distilled off. The distillate contained an oil which is neutral and smells strongly of thioaldehyde, but in which not a trace of nitroethane could be detected by means of the very delicate ethylnitrolic acid reaction.

As mentioned above, nitroethane-mercuric-chloride is decomposed by addition of dilute hydrochloric acid into nitrous oxide and acetaldehyde; the reaction is accompanied by a decided evolution of heat, and a greenish-colored solution is obtained. The quantitative determina-

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\* Ann. Chem. (Liebig), CLXXI. 31.

tions were carried out in the same apparatus as that used above in the case of the sodium salt. The mercury salt is placed in the distilling flask, and 10–15 c.cm. water added; after removing the air, dilute hydrochloric acid is added by means of the separatory funnel, and the solution is then heated to boiling. In the case of the aldehyde determination, the distillate is treated with powdered calcic carbonate, in order to remove the hydrochloric acid carried over, and then redistilled.

1 gram salt gave 39 c.cm.  $N_2O$  at  $23^\circ$  and 748 mm., corresponding to 98 per cent of the theory.

1 gram salt gave 38 c.cm.  $N_2O$  at  $22^\circ$  and 748 mm., corresponding to 95.6 per cent of the theory.

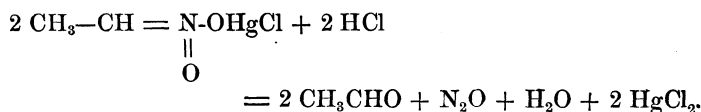
4.5 grams salt gave 1.77 grams silver acetate, i. e. 72.9 per cent of the theoretical amount.

The analysis of the silver acetate, recrystallized from water, gave the following result.

0.3831 gram substance gave 0.2468 gram silver.

	Theory for $CH_3CO_2Ag$ .	Found.
Ag	64.67	64.42

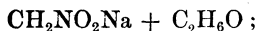
Nitroethane-mercuric-chloride has thus been split by the acid, chiefly according to the following equation:



Nitrous acid and hydroxylaminehydrochloride (0.4 gram crude salt from 10 grams) are side products formed in this decomposition.

*Decomposition of Sodic Nitromethane by means of Acids.*

Sodic nitromethane can be obtained from nitromethane by treating it in absolute ethereal solution with sodium wire, or by means of alcoholic sodic hydrate according to the method of V. Meyer. It is, however, best formed by addition of an alcoholic solution of sodium ethylate to an alcoholic solution of nitromethane. 30 grams nitromethane yield thus regularly from 45 to 50 grams of the sodium salt, which at first contains, as V. Meyer has shown, one molecule of alcohol,

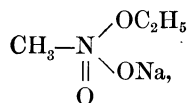


the salt slowly loses its alcohol on standing over sulphuric acid in a vacuum, but never completely. An analysis of a salt, which had been kept 14 hours in a desiccator, gave the following figures

0.2500 gram gave 0.1791 gram  $\text{Na}_2\text{SO}_4$ .

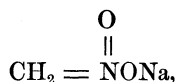
	Theory for $\text{CH}_2\text{NO}_2\text{Na}$ .	Theory for $\text{CH}_2\text{NO}_2\text{Na} + \text{C}_2\text{H}_6\text{O}$ .	Found.
Na	27.71	17.83	23.21

The constitution of this alcoholate is very probably



formed by the addition of the sodium ethylate to the nitro group.

Sodic nitromethane, free from alcohol,



which is best obtained by treating nitromethane in ethereal solution with sodium, is a very unstable and remarkable body, which seems to exist only under great tension. On adding a small amount of water to it, spontaneous decomposition, with tremendous evolution of heat and oftentimes explosion, takes place.\* On allowing an aqueous solution of the salt to evaporate spontaneously, it is decomposed chiefly into sodic carbonate and sodic nitrite (besides other products). The alcoholate of sodic nitromethane is much more stable than the pure sodium salt, but behaves otherwise in an entirely analogous manner. On adding an aqueous solution of either of these salts to dilute sulphuric acid or hydrochloric acid, decomposition into nitrous oxide, formaldehyde, nitrous acid, carbonic acid, and hydroxylamine takes place, and *not a trace of nitromethane is regenerated*.

The amount of nitrous oxide formed is small, as is evident from the following determinations.

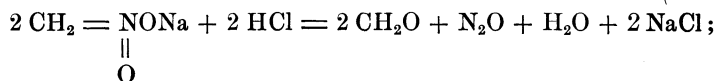
2 grams sodium salt, made by means of sodium ethylate and kept a long time in a vacuum, gave 20 c.cm.  $\text{N}_2\text{O}$  at  $20^\circ$  and 752 mm., corresponding to 7.44 per cent of the theory for  $\text{CH}_2\text{NO}_2\text{Na}$ .

3 grams sodium salt, made by means of sodium ethylate and used directly, gave 26 c.cm.  $\text{N}_2\text{O}$  at  $22^\circ$ , and 748 mm., corresponding to 7.48 per cent of the theory for  $\text{CH}_2\text{NO}_2\text{Na} + \frac{1}{2} \text{C}_2\text{H}_6\text{O}$ .

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\* Ann. Chem. (Liebig), CLXXI. 34.

In the decomposition of sodic nitromethane by acids, a splitting takes place, but in subordinate amount, according to the equation



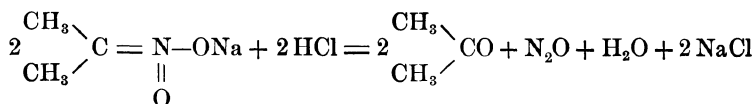
which is entirely analogous to the decomposition of nitroethane salts. The reason for this difference is also perfectly clear and will be explained farther on.

It is possible, but only under very special conditions and in subordinate amounts, to regenerate nitromethane from its sodium salt;\* in all cases a very decided decomposition takes place, as will become evident from the following experiments. 10 grams sodic nitromethane, made by means of sodium ethylate and kept 10 hours in a vacuum over sulphuric acid, are dissolved in water containing pieces of ice, and then dilute sulphuric acid is added very slowly. As soon as the solution becomes acid, a smell of formaldehyde is noticed, as well as the presence of nitrous acid and of nitrous oxide and carbon dioxide. 20 c.cm. of the solution † is then distilled off (until no smell of nitromethane can be noticed in the flask) and the distillate extracted with ether. The ethereal solution, carefully fractionated, gave 1.9 grams nitromethane, boiling between 99° and 101°. An entirely analogous result is obtained from a solution of nitromethane in caustic soda or potash.

*Decomposition of Secondary Sodic Nitropropane by Acids.*

Secondary nitropropane was made according to the directions of V. Meyer.‡ The yield is very poor. The sodium salt was made by means of alcoholic sodium ethylate, and dried over sulphuric acid in a vacuum.

On treatment of an aqueous solution of this salt with dilute acids, a fairly smooth decomposition into acetone and nitrous oxide, according to the equation



takes place, — a reaction which is perfectly analogous to the decomposition of salts of primary nitroparaffines.

\* No statements concerning this point could be found anywhere.

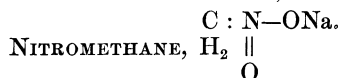
† Preibisch, Journ. f. prakt. Chemie, [2.], VIII. 311.

‡ Ann. Chem. (Liebig), CLXXI. 40

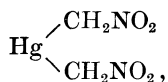
0.7 gram sodium salt, dissolved in water and added in the above apparatus to 15 c.cm. dilute sulphuric acid, gave (the solution becomes colored greenish) 51 c.cm.  $N_2O$  at  $21^\circ$  and 754 mm., corresponding to 66.52 per cent of the theory.

The formation of acetone in this reaction was proved as follows. 1.9 grams secondary sodic nitropropane are dissolved in water and added to 15 c.cm. dilute sulphuric acid. The bluish green solution is heated to boiling and partially distilled off. The distillate is filtered from a small amount of solid and treated with powdered calcic carbonate and then redistilled. The solution thus obtained, which smells distinctly of acetone, is treated with a solution of 0.6 gram hydroxylamine hydrochloride and 0.34 gram caustic soda in 2.5 c.cm. water. After standing for an hour, the solution is extracted three times with ether, and after getting rid of the dried ether 0.35 gram residue is obtained. This was recrystallized from ligroine (bpt.  $40^\circ$ – $60^\circ$ ) and found to melt at  $62^\circ$ – $63^\circ$ , and to consist of pure acetoxime, identical in every respect with a product made for comparison.

## II. SYNTHESIS OF MERCURY FULMINATE, $C:NOhg$ , FROM SODIC



With the exception of nitroethane-mercuric-chloride, no heavy metal salt of a simple nitroparaffine has been obtained and analyzed. Victor Meyer and Rilliet obtained from sodic nitromethane and mercuric chloride a yellow very explosive mercury salt, which they regarded as mercury nitromethane,



but which, on account of its very dangerous properties,\* was not further investigated or analyzed.

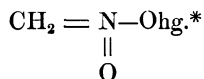
Since such heavy metal salts might perhaps be especially well adapted for a determination of the constitution of the nitroparaffine salts, a study of this salt was therefore again taken up, and it soon became evident that it is not a salt of nitromethane at all because it contains no hydrogen.

On adding quickly an aqueous solution of sodic nitromethane to a solution of corrosive sublimate, or *vice versa*, a white precipitate is first

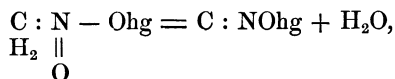
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\* Ber. d. chem. Ges., V. 1030. Cf. Ann. Chem. (Liebig), CLXXI. 35.

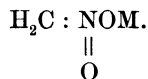
formed, which very soon becomes colored yellow, and which in all probability is the mercury salt of nitromethane,



This white salt exists, however, only a few moments, since it is a very powerful oxidizing agent capable of intra-molecular oxidation. It therefore loses water almost instantly,



forming mercuric fulminate; and since the constitution of fulminate of mercury is definitely proved in the following paper to be  $\text{C} : \text{NOhg}$ , it follows at the same time that the nitromethane salts must have the constitution represented by the general formula



An aqueous solution of sodic nitromethane (10 grams) is added rapidly to a cold mercuric chloride solution (containing 16 grams  $\text{HgCl}_2$ ). After standing 15 minutes, the solution (300–500 c.cm.) is heated to boiling and quickly filtered from the yellow precipitate, which is then boiled out once with hot water. On cooling, a grayish white heavy crystalline precipitate separates out from the filtrate. In order to get rid of traces of adhering mercury, it is dissolved in dilute cyanide of potash and reprecipitated with dilute nitric acid.† In this way perfectly pure fulminate of mercury is obtained, which is absolutely identical in every respect with the product made in the ordinary way. The yield is 1 gram to 1.6 grams pure salt from 10 grams sodic nitromethane.

0.2221 gram substance, dried over  $\text{H}_2\text{SO}_4$  in a vacuum, and dissolved in dilute hydrochloric acid, with addition of  $\text{KClO}_3$ , and precipitated with  $\text{H}_2\text{S}$ , gave 0.1815 gram  $\text{HgS}$ .

0.4005 gram substance, mixed with cupric oxide, gave 0.1248 gram  $\text{CO}_2$  and 0.0074 gram  $\text{H}_2\text{O}$ .

0.1968 gram substance gave 17.5 c.cm.  $\text{N}_2$  at  $16^\circ$  and 747 mm.

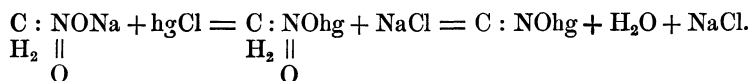
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\* hg represents a half-atom of bivalent mercury.

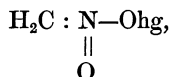
† Steiner, Ber. d. chem. Ges., IX. 787.

	Theory for HgO <sub>2</sub> N <sub>2</sub> C <sub>2</sub> .	Found.
Hg	70.42	70.45
C	8.45	8.49
H	—	0.205
N	9.86	10.18

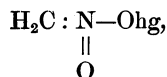
The following very simple reaction therefore takes place in the formation of mercuric fulminate from sodic nitromethane:



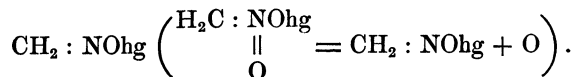
It follows clearly, however, that the mercury salt of nitromethane,



formed as the intermediate product, must be a strong oxidizing agent, which at first, for want of anything else present, acts on itself, forming by intra-molecular oxidation fulminate of mercury, C : NOhg. Since, however, the fulminate of mercury thus formed, in consequence of its containing unsaturated or bivalent carbon, possesses an enormous reactivity (see following paper) and can therefore most readily take up oxygen, (this explains the reducing action of carbon monoxide, C : O, of cyanide of potash, KN : C, as well as of the fulminates, C : NOM,) it follows very clearly that the strong oxidizing agent present, mercury nitromethane,

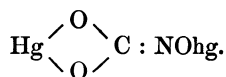


can act also on the mercury fulminate formed (in the nascent state), converting it into mercuric carbondioxidoxime, O : C : NOhg, whereby the mercuric nitromethane itself is reduced to mercuric formoxime,

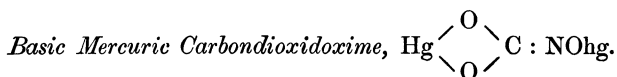


This explanation suffices completely in clearing up the nature of all the products which are formed by the interaction of sodic nitromethane and mercuric chloride. The yellow salt obtained by V. Meyer

and Rilliet\* is, in all probability, basic mercuric carbondioxidoxime,



A yellow compound insoluble in water is, in all cases, the chief product of the action between aqueous solutions of sodic nitromethane and mercuric chloride; in fact only by the above mentioned method is it possible to obtain fulminate of mercury in appreciable amounts. If the corrosive sublimate solution is heated, before adding the sodic nitromethane solution, or if the former solution is added to the latter solution, not a trace of mercuric fulminate can be isolated, and much yellow insoluble mercury salt is formed. The composition of this yellow salt varies also according to whether the mercuric chloride solution is added to a solution of the sodium salt, or *vice versa*. In the latter case, the salt obtained contains much more carbon and nitrogen.



On the addition of a solution of mercuric chloride (containing 16 grams  $\text{HgCl}_2$ ) to a cold aqueous solution of sodic nitromethane (10 grams), a white precipitate is formed which, after an hour's standing, has become perfectly yellow. The solution is decanted, and the residue is repeatedly treated with boiling water, and then dried on clay plates, and finally at  $100^\circ$ . The latter operation must be carried on with all possible precautions, since it happened several times that the salt exploded, demolishing the air bath and the windows of the hood. The yield from 10 grams sodium salt was regularly from 8 to 10 grams. The salt is, at ordinary temperatures, not quite so dangerous as mercuric fulminate, but it often explodes by friction. It is absolutely free from chlorine and contains no hydrogen: digestion with dilute sulphuric or with dilute nitric acid, in which it is insoluble, does not change the composition of the salt.

0.4698 gram, mixed with cupric oxide, gave 0.0612 gram  $\text{CO}_2$  and 0.0129 gram  $\text{H}_2\text{O}$ .

0.1818 gram, mixed with cupric oxide, gave 6.5 c.cm.  $\text{N}_2$  at  $19^\circ$  and 747 mm.

0.2195 gram, dissolved in dilute hydrochloric acid, with addition of little  $\text{KClO}_3$  and precipitated with  $\text{H}_2\text{S}$ , gave 0.2045 gram  $\text{HgS}$ .

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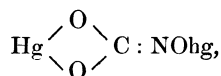
\* Ber. d. chem. Ges., V. 1030. Cf. Ann. Chem. (Liebig), CLXXI. 35.



	Theory for $\text{Hg} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{C} : \text{NOhg}$	Found.
C	3.21	3.34
H	—	0.305
N	3.74	4.04
Hg	80.20	80.31

The salt is instantly decomposed by dilute hydrochloric acid, forming calomel, carbonic acid, and a substance having a smell like prussic acid, but not a trace of nitrous oxide is formed. Concentrated hydrochloric acid decomposes the salt into carbonic acid and hydroxylaminehydrochloride (proved by conversion into acetoxime). The salt is very soluble in dilute cyanide of potash, and on addition of dilute nitric acid no precipitate is formed. It was at first long suspected that the salt was basic fulminate of mercury, but it is not possible in any way to convert this salt into normal fulminic acid salts. Thus a large quantity of it was added to hydrochloric acid (one part conc. acid 1.18 to one part water), and the solution thereupon extracted with ether; but not a trace of formylchloridoxime (see following paper) was obtained. On treating the salt suspended in water with sodium amalgam, mercury is formed, and a solution obtained free from mercury, in which, however, not a trace of sodium fulminate could be detected.

That the salt possesses the constitution,



is very probable, but not yet proved with absolute certainty. It will therefore be further investigated, especially since its behavior towards alkyl iodides and its conversion into carbondioxidoxime,  $\text{O} : \text{C} : \text{NOH}$ , may be of interest.

As mentioned above, there is formed, on addition of aqueous sodic nitromethane to a mercuric chloride solution, besides fulminate of mercury, a yellow insoluble salt, which is richer in carbon and in nitrogen than the yellow salt just described.

This yellow salt, precipitated from hot mercuric chloride solution, was repeatedly digested with boiling water and then dried, first on a clay plate, and then *carefully* at  $100^\circ$ .

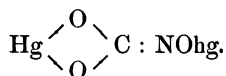
The substance is likewise free from chlorine and hydrogen and explodes very readily by friction.

0.6731 gram, mixed with cupric oxide, gave 0.1487 gram  $\text{CO}_2$  and 0.0236 gram  $\text{H}_2\text{O}$ .

0.2776 gram gave 16 c.cm.  $\text{N}_2$  at  $15^\circ$  and 749 mm.

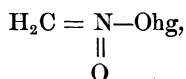
	Theory for $\text{Hg} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix} \text{C} : \text{NOhg}$	Theory for $\text{O} : \text{C} : \text{NOhg}$	Found.
C	3.21	7.59	6.03
H	—	—	0.39
N	3.74	8.86	6.65

This salt behaves in every respect — towards dilute nitric, hydrochloric, and sulphuric acid, towards concentrated hydrochloric acid, sodium amalgam, and cyanide of potash — in exactly the same manner as the mercury salt just described. It probably consists therefore of a mixture of much mercuric carbondioxidoxime,  $\text{O} : \text{C} : \text{NOhg}$  and of the basic salt,

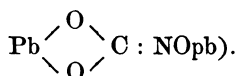


It is natural that in this case much less basic salt should be formed than in the former case, where the corrosive sublimate solution was added to the sodic nitromethane solution.

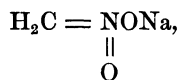
The above experiments have made it clear that the heavy metal salts of nitromethane, e. g. a mercury salt,



are not capable of existence, but are immediately decomposed by intramolecular oxidation. An investigation of the precipitates formed by adding copper sulphate or lead acetate to an aqueous solution of sodic nitromethane showed that these consist in great part either of copper carbonate or of lead carbonate (the lead salt obtained is yellow and explodes, and probably contains some

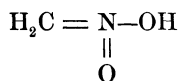


For these reasons it is obvious that sodic nitromethane itself,



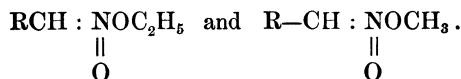
which, as is known, exists only under great tension, must be a strong oxidizing agent which can easily, by intra-molecular oxidation, go over into  $O : C : NONa$  and  $CH_2 : NONa$ ,\* which products in turn are readily split into carbonic acid, hydroxylamine nitrous acid, and other compounds. This explains therefore most clearly the intensely violent decomposition of this salt on addition of a small quantity of water, as well as its decomposition, in dilute aqueous solutions, into sodic carbonate, sodic nitrite, and other products.

On adding sodic nitromethane to dilute acids, the product



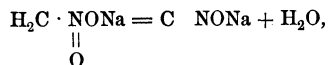
is in all probability first formed, which must readily go over, by intra-molecular oxidation, into  $O : C : NOH$  and  $CH_2 : NOH$ , or into their decomposition products. A slight decomposition, however, into  $2 CH_2O$  and  $N_2O$  also takes place, — which in the case of the other primary and the secondary nitroparaffine salts is the chief reaction (see above).

The formation of the above mentioned remarkable decomposition products of nitroparaffine salts, which, as is clearly seen, is due solely to intra-molecular oxidation, find further on their complete analogy in the decomposition products of esters of the formula,



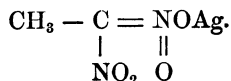
These substances also decompose (some spontaneously) by intra-molecular oxidation into  $RCH : NOH$  and  $CH_3CH : O$  or  $CH_2O$ .

\* The fulminate of soda,  $C : NONa$ , which is first formed as an intermediate product,



must naturally be converted immediately by the excess of sodic nitromethane present into  $O : C : NONa$ , and thus it in turn be reduced to  $CH_2 : NONa$ . It was not possible at any rate, under any condition, to convert sodic nitromethane by loss of water into sodium fulminate, — a fact which in view of the enormous tendency of this salt to take up oxygen is almost self-evident.

## III. THE ACTION OF ALKYLIODIDES ON SILVER DINITROETHANE,



*Preparation of Dinitroethane.* — After many experiments, the following method of preparing dinitroethane was found to give the best results.\* 50 grams bromnitroethane (bpt. 140–145°, prepared according to the directions of Tscherniak †), 50 c.cm. alcohol, and a solution of 56 grams potassic nitrite in 56 grams water, were kept shaken up very thoroughly in a shaking apparatus for 24 hours. The potassium salt of dinitroethane separates out slowly in yellow crystals, which, when filtered off and well washed with alcohol, are sufficiently pure. The yield is from 13 to 14 grams. The salt is dissolved in warm water and treated directly with silver nitrate (one molecule), and the silver salt obtained in glistening heavy yellow leaflets, which are filtered off and dried in a vacuum.

Ter Meer ‡ has already studied the behavior of this salt towards methyl iodide and obtained thereby an oil, which, on treatment with alcoholic potash, is partially converted back again into potassic dinitroethane. Very recently Duden has studied the behavior of silver dinitromethane towards alkyl iodides, § and shown that, for example, it is converted by means of methyl iodide into dinitroethane.

The reaction which takes place, however, on treating the silver salt of dinitromethane and of dinitroethane with alkyl iodides, is far more complicated than either Ter Meer or Duden have surmised; the very remarkable and peculiar reaction is cleared up fully by the following experiments.

50 grams silver dinitroethane are added slowly to 100 grams methyl iodide, taking care to cool well with water. Reaction quickly takes place, with formation of silver iodide, and, towards the end, a strong smell of formaldehyde is noticed. After standing one hour, ether is added and the excess of methyl iodide as well as the ether is removed from the filtrate by heating in a distilling flask at 50 mm. pressure to a temperature of 50°. The residual oil is taken up with ether, and treated with cold dilute sodic hydrate and the deep red colored alkaline solu-

\* Ter Meer, Ann. Chem. (Liebig), CLXXXI. 6; Chancel, Jahresber., 1883, p. 1039.

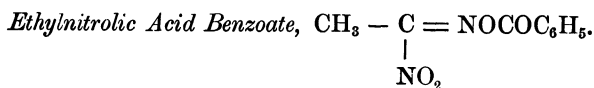
† Ann. Chem. (Liebig), CLXXX. 126.

‡ Ibid., CLXXXI. 16.

§ Ber. d. chem. Ges., XXVI. 8003.

tion immediately acidified with dilute sulphuric acid and extracted with ether. After drying the ethereal solutions with calcic chloride, and getting rid of the ether at reduced pressure, 10.1 grams of neutral products and 9 grams of acid products are obtained.

On allowing the oily acid portion to stand in the air, crystals of ethylnitrolic acid (1 gram) separated out, and the oil gave, on treatment with alcoholic potash, 5.3 grams of potassic dinitroethane, which was filtered off. The deep red colored filtrate gave, on acidifying and extracting with ether, 0.4 gram more of ethylnitrolic acid. The acid products formed in the above reaction are therefore dinitroethane and ethylnitrolic acid. The latter substance melted at 88°, and was identical in every respect with a preparation made from nitroethane.\* This substance gives on treating in alkaline solution with benzoylchloride † a characteristic insoluble benzoate.



12.1 grams ethylnitrolic acid, dissolved in 46 c.cm. sodic hydrate (1 : 10), and shaken with 16.4 grams benzoylchloride gave 21.6 grams crude benzoate (calculated 24.2 grams). Crystallized twice from benzene, and twice from alcohol, it is obtained in colorless flat needles, melting at 135°; it is easily soluble in hot benzene and alcohol, and very slightly in ether. It is insoluble in water, and is decomposed slowly on standing with sodic hydrate into benzoic acid and ethylnitrolic acid.

0.1585 gram, dried at 70°, gave 0.3001 gram CO<sub>2</sub> and 0.0604 gram H<sub>2</sub>O.

0.1995 gram, dried at 70°, gave 24 c. cm. N<sub>2</sub> at 16° and 750 mm.

	Theory for C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub>	Found.
C	51.92	51.64
H	3.85	4.23
N	13.46	13.84

The above mentioned portion (10.1 grams), insoluble in alkalies, is also a mixture of two substances. It was first distilled with steam, whereby all but a trace of yellow sticky material is easily carried over; the first portions of the distillate contain oil drops, which do not solidify, and the latter portions contain a substance which solidifies in

\* Ann. Chem. (Liebig), CLXXV 94; CLXXXI. 2.

† Baumann and Udransky, Ber. d. chem. Ges., XXI. 2744.

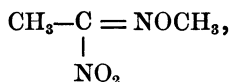
the condenser, so that it is possible already at this point to accomplish a partial separation of the two products. The distillate was, however, extracted with ether; and the ethereal solution was washed with dilute sodic hydrate, and, after drying with calcic chloride, the ether was distilled off. 9.2 grams of oil were obtained, which was fractioned under reduced pressure. The first portions boiled between  $78^{\circ}$  and  $85^{\circ}$  at 30 mm. pressure and were oily; as soon as the distillate begins to solidify, the operation was discontinued, and the residue in the distilling flask (4.25 grams) poured out. On cooling, this solidified completely. It was transferred to a clay plate, and washed with a small amount of ligroine, and thus 2.8 grams perfectly pure  $\beta$  dinitropropane, melting at  $55^{\circ}$ , were obtained, identical in every particular with the product obtained by V. Meyer and Locher.\*

0.2185 gram, dried over  $\text{H}_2\text{SO}_4$  in a vacuum, gave 0.2141 gram  $\text{CO}_2$  and 0.0941 gram  $\text{H}_2\text{O}$ .

0.2272 gram gave 43.5 c.cm.  $\text{N}_2$  at  $24^{\circ}$  and 753 mm.

	Theory for $(\text{CH}_3)_2 : \text{C}(\text{NO}_2)_2$ .	Found.
C	26.86	26.72
H	4.48	4.79
N	20.90	21.27

The lower boiling oil, which is not volatile without decomposition at ordinary pressure, and which is more volatile with steam than  $\beta$  dinitropropane, was not analyzed, as it still contained traces of  $\beta$  dinitropropane. That it consists, however, of ethylnitrolic acid methylester,



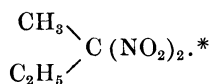
is very probable, and a number of experiments were therefore carried out with the object of isolating this substance directly from the silver and lead salts of ethylnitrolic acid by means of methyl iodide, which, however, failed on account of the great instability of the ethylnitrolic acid salts in the presence of water.†

On adding 11 grams of silver dinitroethane to 50.5 grams ethyl iodide, reaction sets in immediately, and at the end a very strong smell of acetaldehyde is noticed. Both neutral and acid products are formed :

\* Ann. Chem. (Liebig), CLXXX. 147.

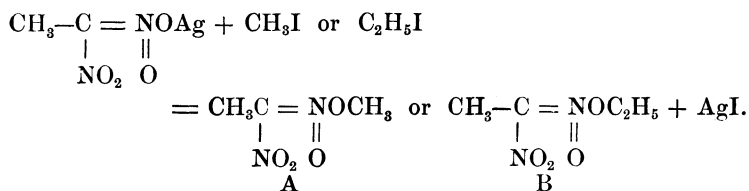
† V. Meyer, Ann. Chem. (Liebig), CLXXV. 103.

the presence of ethylnitrolic acid and of dinitroethane in the acid portion was proved as in the above case. The neutral portion was an oily mixture, boiling between  $105^{\circ}$  and  $130^{\circ}$  at 30 mm. pressure. The amount of material at hand was, however, insufficient to admit of its further study, although a portion boiled at ordinary pressure at about  $200^{\circ}$ , and consists therefore probably of  $\beta$  dinitrobutane,

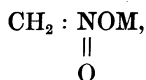


The results obtained above prove that the reaction which takes place on treating silver dinitroethane with alkyl iodides is the following.

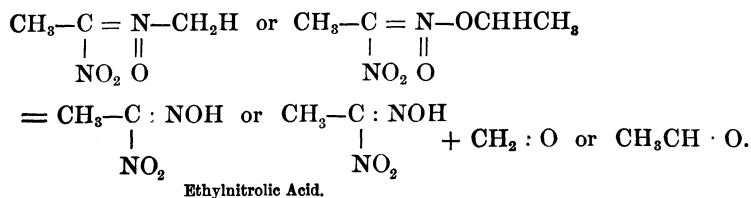
I. Direct replacement of the metal (chief reaction) :



The esters A and B, which are first formed, are however very unstable compounds, and just as the nitromethane salts,

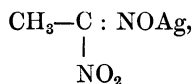


are strong oxidizing agents. An intramolecular oxidation therefore takes place, and ethylnitrolic acid and either formaldehyde or acetaldehyde is formed, according to the equation :

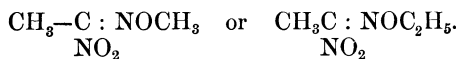


The ethylnitrolic acid thus formed reacts upon silver dinitroethane, present in excess, setting free dinitroethane and forming the silver salt of ethylnitrolic acid,

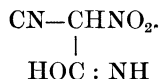
\* V Meyer, Ber. d. chem. Ges., IX. 701.



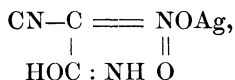
which then reacts with the iodide of methyl or ethyl, forming either the methyl ester or the ethyl ester of ethylnitrolic acid,



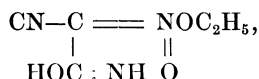
That this explanation of the reaction is the correct one, is proved with certainty by the following fact: fulminuric acid is, as will be shown in the paper presented directly after this one, identical with nitrocyanoacetamide,



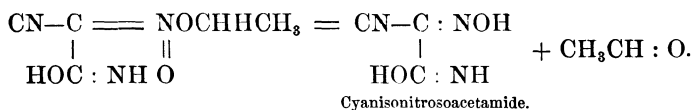
On treating the silver salt of this substance,



with ethyliodide, there is formed, by direct replacement of the silver, the ester,



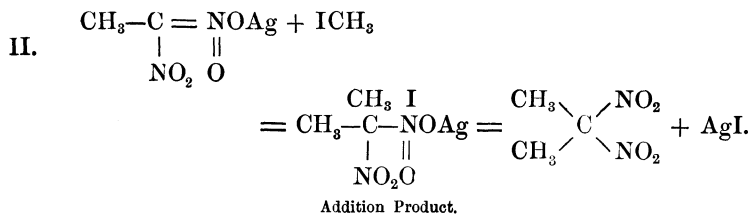
which, in this case, can be isolated. This compound is, however, very unstable, and shows, just as the above assumed intermediate products (A and B) and as the nitromethane salts, great tendency to intramolecular oxidation. On boiling with water it is split quantitatively into acetaldehyde and cyanisonitrosoacetamide (see following paper).



This decomposition is perfectly analogous to those above.

The formation of  $\beta$  dinitropropane from silver dinitroethane and methyl iodide is in all probability to be explained by an addition of methyl iodide to the silver salt of dinitroethane :





There are now so many cases known, where, by the interaction of silver salts with alkyl iodides or acid chlorides, no direct or only partially a direct replacement of the silver takes place,\* that this explanation is not at all improbable, — especially also when one considers the remarkable behavior of silver fulminate towards hydrogen sulphide and towards hydrochloric acid (see following paper).

The formation of formic aldehyde, ethylnitrolic acid, dinitroethane,  $\beta$  dinitropropane and of a fifth compound, probably ethylnitrolic acid methylester, on treating silver dinitroethane with iodide of methyl, is therefore perfectly cleared up by the above considerations.

#### IV. THE ACTION OF ACID CHLORIDES ON NITROPARAFFINE SALTS.

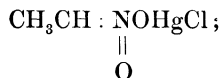
The former experiments on the action of acetylchloride and of benzoylchloride on sodic nitromethane and on sodic nitroethane† have led to no positive results. Kissel has shown‡ that in these reactions some dibenzhydroxamic acid and diacethydroxamic acid is formed, but these can only have been formed, however, by a complete destruction of the nitroparaffine molecule.

I have also carried out many fruitless experiments on these salts with acetylchloride and benzoylchloride, and also with chlorocarbonic ether; both neutral and acid products are formed, which cannot be solidified, and which do not distil under reduced pressure without decomposition. Entirely analogous results were obtained by the action of acetylchloride and benzoylchloride on nitroethane-mercuric-chloride,

\* Ann. Chem. (Liebig), CCLXX. 329, 331; CCLXXVI. 232; CCLXXVII. 73. The experiment with silver acetylacetone has been carried out here by Dr. Curtiss with larger quantities of material, and both products have been analyzed.

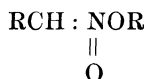
† V. Meyer and Rilliet, Ber. d. chem. Ges., V. 1030; VI. 1168.

‡ Ber. d. chem. Ges., XV. Ref. 727 and 1574.

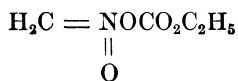


both these reagents, and especially the former, act with explosive violence on this salt, so that it is necessary to dilute with absolute ether.

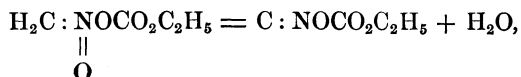
The above results with silver dinitroethane, which have shown that neutral ethers of the constitution



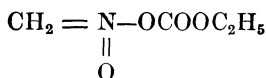
must be strong oxidizing agents, encourage one to undertake a renewed study of the action of acid chlorides on nitroparaffine salts, and experiments will therefore very shortly be taken up again. Of especial interest is the behavior of chlorocarbonic ether towards sodic nitromethane. It is to be expected that the ester



will at first be formed, and this compound must, by intramolecular oxidation, lose water, and be converted into carbyloximecarbonic ester,



which then will be further oxidized by the ester



to carbondioxydoximecarbonic ester,  $\text{O} : \text{C} : \text{NOCO}_2\text{C}_2\text{H}_5$ , and at the same time thus formoximecarbonic ester,  $\text{CH}_2 : \text{NOCO}_2\text{C}_2\text{H}_5$ , will be formed.

#### CONCLUDING REMARKS.

The above experiments suffice to prove, with absolute precision, that the metal in the nitroparaffine salts is bound to oxygen, and not, as has been previously supposed, to carbon; and in consequence, the hypothesis that there are organic substances of an acid nature, in whose salts the metal is bound to carbon, is no longer tenable. Its

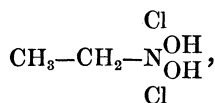
conception has been shown to be illogical,\* and the work that I have carried out during the last six years has proved, by incontrovertible experimental evidence, the erroneousness of this hypothesis in all cases where it has been applied.

The only instances of organic compounds now known which contain a metal bound directly to carbon are the metallic carbides, the metallic alkyls, and the metallic derivatives of the true acetylene compounds. No one would however be willing to assert that these substances are salts of acids. Acetylene, for example, is not an acid, for it is not absorbed with salt formation by even concentrated caustic alkalies. The peculiar formation of the metallic acetylene derivatives, e. g. of acetylene silver or copper, depends, in all probability, upon an addition of metallic hydroxide to the triple bond present in acetylene, and the subsequent splitting off of water.

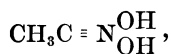
As regards the constitution of the free nitroparaffines, the presence of a true nitro group in these compounds can hardly be seriously questioned, especially in view of the experiments of Victor Meyer † and the late syntheses carried out by Bewad. ‡

The formulæ suggested for nitroethane by Geuther, § Kissel, || Alexejeff, ¶ and Thomsen, \*\* owe their existence chiefly to the very noteworthy decomposition of nitroethane into acetic acid and hydroxylamine, when treated with concentrated hydrochloric acid. ††

This decomposition of nitroethane can now, because of the above experiments, be easily explained. An addition of hydrochloric acid to the nitro group, analogous to the addition of sodic hydrate or sodium ethylate, first takes place, forming



which then loses hydrochloric acid



\* These Proceedings, XXVII. 157.

† Ann. Chem. (Liebig), CLXXI., etc.

‡ Journ. f. prakt. Chemie, [2.], XLVIII. 346.

§ Ann. Chem. (Liebig), CCXLIII. 105.

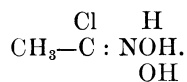
|| Journ. russ. chem. Soc., XIV. 40.

¶ Ber. d. chem. Ges., XIX. Ref. 874.

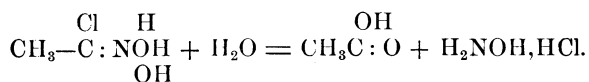
\*\* Journ. f. prakt. Chemie, [2.], XLVIII. 348.

†† V. Meyer and Locher, Ann. Chem. (Liebig), CLXXX. 168.

and then again adds hydrochloric acid



This product can then easily split into acetic acid and hydroxylamine,



In the above experiments I have been most ably and zealously assisted by Dr. M. Ikuta, to whom I wish here also to express my warmest thanks.